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Spray-pyrolysis or spray-drying process, and plant for carrying it out

The present invention relates to an improved spray-pyrolysis or spray-drying process for the preparation of inorganic oxides and mixed oxides or powder materials, and to a plant for carrying out the process.

Many pigments (for example TiO_2), ceramics (SiO_2, A1203) and specialty chemicals (ZnO_2) are nowadays produced in an amount in the order of a few million tonnes per year by flame aerosol technology [1]. A special form of flame aerosol technology is spray pyrolysis, in which a precursor salt solution is finely atomized, for example, directly into a flame or into the hot combustion gases of a flame. During this operation, first the solvent, for example, water, evaporates. The crystallized-out salts are then thermally decomposed in such a way that either a metal oxide remains as solid residue (for example on decomposition of nitrates) or the metal ion formed during decomposition is oxidized by gaseous oxygen. In other processes, the disperse products are synthesized from gaseous starting materials in a hot atmosphere, for example in a plasma. In all cases, extremely fine solid particles are formed, which are separated off from the gas stream by a dust separator and recovered as product. Quality features of the powders here are, inter alia, an extremely well-defined particle size distribution, an extremely high degree of dispersion, an extremely precise stoichiometry of multi-component products, and a content of "hard agglomerates" which approaches zero as closely as possible, it being possible to influence these features, for example, through the atomizer system and the reaction conditions, in particular the temperature.

During transport, the particles can be deposited on the reactor wall by thermophoresis or diffusion from the gas stream and can result in serious operating problems [Pratsinis, S.E.: Flame aerosol synthesis of ceramic powders, in Progress in Energy and Combustion Science 24, No. 3 (1998), 197 - 221].

At present, spray pyrolysis is used for the production of precursor powders for the preparation of high-temperature superconductors by a process which is described, for example in DE 39 16 643 C1. This and similar processes have the following problems in operation:

1. Pulverulent deposits on the reactor wall must be removed at intervals in time, which means that operation of the plant must be interrupted.

2. Owing to the spraying into a flame which has different temperature zones, the solution droplets react under different conditions. This reduces the quality of the product (stoichiometry, hard agglomerates).

3. Due to the broad size distribution of the droplets, which is determined by the atomizer system, the particle size distribution of the product produced as a powder is also broad and has a proportion of oversized particles which, under certain circumstances, reduces the product quality.

It is therefore an object of the invention to provide a process which does not have the said disadvantages. At the same time, it is also an object of the invention to provide an apparatus by means of which on the one hand deposits on the walls of the plant are avoided, and which simultaneously enables the production of an extremely agglomerate-free product which has a defined

particle size distribution and a homogeneous stoichiometric composition.

The object is achieved by a spray-pyrolysis or spray-drying plant, which can be constructed vertically or horizontally and is distinguished by the fact that
a) a reaction tube (1) is accommodated in an outer tube (2) of heat-resistant steel sheeting in such a way that an annular space is formed between the two tubes, where
b) an atomization system (3) is located at one end of the tubes and
c) one or more jacket connectors (5) lead into the annular space,
d) if desired, gas inlet slots or nozzles (6) and (7) at the height of the atomization system lead into the reaction tube,
e) the gas inlet slots or nozzles as in d) can be replaced by various forms of gas burners,
f) the atomization system consists of one or more single- or multi-component nozzles.

The reaction tube in this spray-pyrolysis or spray-drying plant consists of a heat-resistant, porous material.

The invention thus relates to a spray-pyrolysis or spray-drying plant which has a reaction tube of a porous material which is heat-resistant up to 1200°C and which has a pore diameter of from 1 to 5 μm.

The heat-resistant, porous material preferably consists of heat-resistant metal alloys or suitable ceramic materials.

In particular, this material is a heat-resistant sintered metal, metal mesh or metal non-woven medium.

The present invention also relates to a spray-pyrolysis or spray-drying plant whose atomization system consists of a nozzle plate to which the atomization energy is transferred by means of a piezoceramic oscillator, resulting in the formation of a monodisperse drop distribution.

Suitable nozzle plates which can be installed in the plant according to the invention are nozzle plates with holes having a diameter of from 10 to 40 μm.

In particular, the invention relates to a reaction tube consisting of a gas-permeable, porous material which is heat-resistant up to 1200°C and has a pore diameter of from 1 to 5 μm.

The spray-pyrolysis or spray-drying process is carried out in accordance with the invention by passing gas through a jacket connector (5) into an annular space formed by a reaction tube (1) and an outer tube (2), with the introduced gas flowing through the porous material of the reaction tube into the reaction space, resulting in the formation of a gas stream away from the jacket surface, which in turn prevents deposition of formed particles on the surface.

Furthermore, a solution or suspension of a metal salt or a mixture of metal salts or a metal salt solution which comprises suspended, insoluble particles of a metal-containing compound, for example metal oxides, is introduced in the desired stoichiometric ratio by means of an atomization system (3), for example consisting of a nozzle plate, to which the atomization energy is transferred by means of a piezoceramic oscillator, in finely divided form in the form of a monodisperse spray into the reaction tube (1), where it encounters the optionally preheated gas flowing in through the porous wall of the reaction tube and is either dried in the

gas stream to form a powder having a uniform particle size distribution and is discharged at the end of the reaction tube together with the gas stream, or
is caused to decompose or react in the gas stream by supply of additional process energy, where the reaction may be exothermic, and the reaction product formed is discharged at the end of the reaction tube as a finely divided powder together with the gas stream.

In a particular embodiment of the process according to the invention, the wall of the reaction tube is cooled constantly during the exothermic reaction by the gas passing through from the outside.

Furthermore, if necessary, additional process energy can be supplied during performance of the process according to the invention by burning a gas with an oxidant, where either
the air is supplied from the outside via the jacket connector (5) and the gas is added from the inside via gas connectors and inlet slots or nozzles or gas burners (6) and (7), or
the gas is added from the outside (5) and the air is supplied from the inside via gas connectors and inlet slots or nozzles or gas burners (6) and (7), or
the air supplied via the jacket connector (5) is electrically heated, flows through the porous wall and reacts exothermically with the stream of fuel gas added via the gas connector and inlet slots or nozzles or gas burners (6) and (7) and increases the reaction temperature.

The process according to the invention gives powder materials having an average particle size of from 0.1 to 10 μm.

As is already evident from the object, features of the present invention relate, in particular, to changes to

spray-pyrolysis processes which are already known and are aimed at solving the outlined operating problems. In detail, these are the following:

1. The design of the reaction tube as a porous wall through which a gas flows, causing the formation of a gas stream away from the wall and preventing deposition of particles (Fig. 1).

2. The pretreatment and routing of the gases used in the process for specifically influencing the process and the product quality.

3. The use of a known spray system for the preparation of oxidic powders based on single- or multi-component metal oxides, which is characterized in that it produces a very narrow size distribution with very fine droplets, which can favourably influence the product quality.

In accordance with the invention, a tubular reactor made from heat-resistant steel sheeting is replaced by a cylindrical tube made from a porous, stable material accommodated concentrically in a jacket tube. Suitable materials for this purpose can be those used for hot-gas filter cartridges, such as, for example, sintered metal, metal mesh or metal non-woven media. These materials consist of heat-resistant metal alloys having a heat resistance of up to 1200°C. A reaction tube (1) consisting of a material of this type is accommodated in a jacket tube (2) of heat-resistant steel sheeting in such a way that an annular space is formed between the two tubes. The atomizer system (3) is located at one end of the tubes, which are arranged either vertically or horizontally, and the gas outlet (4) is located at the opposite end. The plant according to the invention is preferably constructed vertically, and the atomizer system is installed at the upper end, so that

the product formed can be discharged at the lower end together with the gas stream. By means of a suitable dust separator, for example a filter, electrostatic filter, cyclone or the like, the hot gas stream is freed from the particles formed. The filter system employed can be any desired system which is suitable for this purpose.

A gas introduced into the annular space via connectors (5) flows uniformly through the porous medium through the jacket surface and thus prevents particles from the hot-gas stream from depositing on the wall. The reactor is thus operated with constant cleaning, like a filter cartridge.

The plant thus provided is distinguished over earlier attempts to solve the problems described by a simpler design. For comparison, reference is made here to the plant used in the two patents DE 42 14 725 C2 and DE 42 14 722 C2, in which deposition on the reactor wall is claimed to be prevented by a layer of inert gas. The layer of inert gas is generated by introducing a stream of inert gas through specially shaped annular gaps in the reactor wall, this stream hitting the reactor wall via the coanda effect.

By contrast, the prevention of particle deposition in the plant according to the invention is based on the formation of a flow field directed away from the wall.

The process can be specifically influenced by pretreatment and routing of the process gases. The following possibilities arise here in principle:

1. Pure electrical operation of the process

Electrically preheated gas, for example air treated by an electric air heater, is introduced into the annular

space through the connectors (5) and enters the reaction space through the porous wall.

A plurality of such jacket connectors can be charged, as desired, with gases at different temperatures. If desired, the reaction tube can be specifically segmented in order to be able to influence the temperature profile in the reaction space and also the flow through certain tube segments.

The reaction temperature in this procedure is limited to a maximum of 1200°C owing to the material resistance and can be set freely within these limits.

2. Pure combustion operation

In this case, the process energy is provided by burning a gas (for example natural gas or H_2) with an oxidant (for example air). The reactants here are introduced separately into the reaction tube. When the ignition conditions have been reached, they react exothermically with one another. No problems are caused if the reaction temperature possibly exceeds the maximum material temperature of 1200°C in this procedure, since the reactor wall is constantly cooled by the incoming gas stream. Control of the reaction temperature can take place via the air ratio index of the combustion or via the amount of gas supplied. The following possibilities basically arise for process control:

I. Air supply from the outside through jacket connectors (5), gas supply from the inside via gas connectors and inlet slots or nozzles or gas burners (6), (7).

II. Gas supply from the outside through jacket connectors (5), air supply from the inside via gas

connectors and inlet slots or nozzles or gas burners (6), (7).

If desired, a part-stream of air can additionally be added via the air inlet slots, nozzles or gas burners to the air flowing into the reactor via the jacket in order favourably to influence the combustion of the gases.

3. Combined electrical/combustion operation

This process consists of a combination of the plant operation described under 1. and 2. The stream of air added via the jacket connector (5) can be electrically preheated here. This stream of hot gas can then react exothermically with the stream of fuel gas introduced via the gas connector (6) and the inlet slots, nozzles or gas burner (7) and can thus increase the reaction temperature. This procedure enables both reliable ignition by pre-warming of the oxidant above the ignition temperature as well as regulation of the reaction temperature independently of the air index by influencing the pre-warming temperature electrically.

In principle, the two procedures mentioned under 1 and 2 are possible with pre-warming of air or gas.

A mode of operation as described under 3. has the advantage over that described under 1. that a higher reaction temperature can be achieved. Compared with a mode of operation as under 2., the latter variation has the advantage of more reliable ignition.

Besides the described routing according to the invention of the gas streams, the present plant can be fitted with one or more single- or multi-component nozzles or with a spray system as described in Brenn, G., Heliö, T., Durst, F.: A new apparatus for the production of monodisperse sprays at high flow rates,

in Chemical Engineering Science 52, No. 2 (1997), 237 - 244, and Brenn, G., Durst, F., Tropea, C.: Monodisperse sprays for various purposes - their production and characteristics, in Part. Syst. Charact. 13 (1996), 179 - 185, which is based on the principle of Rayleighian beam splitting due to high-frequency excitation.

This system enables a monodisperse spray to be generated. The atomization energy is transferred through excitation of a nozzle plate with a piezoceramic oscillator with which the liquid column is in contact. The nozzle plate is provided with holes, which can be drilled with laser beams and can have diameters of down to 10 μm. If desired, nozzle plates having different hole sizes can be employed. Those having diameters of from 10 to 40 μm can be employed. However, experience suggests that the product quality is better the smaller the hole diameter of the nozzle plate employed. The drop diameter of the sprayed solution is usually about twice the hole diameter. The minimum drop diameter that can be achieved in this way is thus 20 μm, which is finer than the drops of most conventional nozzle systems. These nozzles therefore have the following advantages for generating spray in spray-pyrolysis processes:

- No atomization gas is necessary.
- A monodisperse drop size distribution is achieved.
- Nozzle patterns drilled in any desired manner can be provided on the nozzle plate.
- Nozzle plates of large area can be employed.
- Sprays having extremely small drop diameters can be generated at high throughputs.

The narrow drop distribution at the same time as small drop diameters has an advantageous effect on the particle size distribution of the product, enabling

extremely fine powder materials having a uniform particle size distribution to be produced.

The variability in the design of the nozzle plate and the fact that the atomization can be achieved without additional gas enables optimum matching of the system to the use of the plant as a spray-pyrolysis plant.

Corresponding experiments have demonstrated the particular suitability of the system described in the production of ceramic powders by spray pyrolysis.
With the given information, it is possible for the person skilled in the art to achieve various variations of the plant described, as needed, which can be run in a wide variety of modes of operation, in each case matched to the desired product. Accordingly, the scope of protection of this invention covers not only the embodiments of the plant and process specifically described in this application, but also their modifications which can be carried out in a simple manner.

Fig. 1 shows a possible embodiment of the plant according to the invention. Plant parts designated by numerals (1) to (7) are the following:
(1) Reaction tube
(2) Outer tube
(3) Atomization system
(4) Gas outlet
(5) Jacket connector
(6) Gas connector
(7) Inlet slots or nozzles or gas burners for reaction gas

Examples

Apparatus and procedure

The apparatus used is a vertically arranged tubular reactor with a length of 200 cm and an external diameter of 40 cm. The reaction tube installed concentrically on the inside has an internal diameter of 20 cm and consists of a sintered powder of a heat-resistant metal alloy (Hastelloy X®). A gas burner which, depending on the mode of operation, can be supplied with fuel gas and combustion air via connectors, is located at the top end. A casing tube, through which an atomization lance can be pushed into the reaction tube, is located in the centre of the burner. At the lower end, the reaction tube leads into a hot-gas filter. The jacket connectors feeding the annular space are provided with electric air heaters, so that the inflowing air can be pre-heated to a maximum of 900°C. The metal-salt solution is sprayed into the pre-heated reactor by means of the atomization lance. The powder obtained is collected in the downstream hot-gas filter.

The metal salt solution to be atomized consisted of nitrates of the elements Pb, Bi, Sr, Ca and Cu, which were dissolved in water with a small amount of nitric acid in the following mixing ratio:

Metal salt	Initial weight [kg/kg]
$Pb(NO_3)_2$	0.022
$Bi(NO_3)_3*5H_2O$	0.155
$Sr(NO_3)_2$	0.079
$Ca(NO_3)_2*4H_2O$	0.095
$Cu(NO_3)_2*3H_2O$	0.145
HNO_3	0.087
Water	0.583

This mixing ratio gives rise to a molar ratio of the metals present in the solution of Pb 0.33, Bi 1.80, Sr

1.87, Ca 2.00 and Cu 3.00. The solution was to be converted into a partially oxidic powder having the same stoichiometry as the Me nitrate solution within narrow limits (deviations < 5% of the theoretically determined stoichiometry) by spraying into the above-described reactor and heating with evaporation of the water and partial decomposition of the metal nitrates. In this way, the aim was to obtain a partially oxidic precursor powder for the preparation of high-temperature superconductors.

Example 1

In three test runs, the Me nitrate solution was sprayed into the reactor using a two-component nozzle at a metering rate of 3.5, 5 and 12.5 kg/h over a period of 8 hours in each case. During this, the reactor was heated exclusively via an electric air heater. The air stream entering the annular space (76 kg/h) was thereby heated to a temperature of 700°C, measured at the upper end of the annular space. The hot air penetrated through the porous reaction tube and mixed with the spray mist, causing the water to evaporate from the droplets and causing the metal nitrate particles formed to partially decompose. The decomposition became evident during the process from the NO_x contents measured in the off-gas from the apparatus. As essential process data, the solution mass flow dm/dt_{soln}, the temperature in the annular space in the upper part of the reactor T_o and the temperature in the pipe connecting the reactor and the hot-gas filter (T_f) were measured. The table below shows the average measurement results.

Test run No.	dm/dt_{soln}	T_o	T_f
1	3.5	700	450
2	5	700	440

3	12	700	380

Investigation of the reaction tube after each test run showed that the tube wall was in each case absolutely free from powder deposits. The powder obtained was investigated for hard agglomerates, morphology, ignition loss and stoichiometry. Since there is no reliable measurement method for the analysis of individual hard agglomerates, a relatively coarse powder sample was coated onto a sheet of paper using a spoon spatula. In the presence of hard, relatively coarse particles, tracks are normally evident in the smoothed powder surface. Since such tracks were not observed, it can be concluded that no hard agglomerates are present in the powder. The remaining analyses are shown in the following table. The stoichiometry is given as the number of moles in accordance with the above empirical formula.

Test run No.	Ignition loss	Pb	Bi	Sr	Ca	Cu
1	27 wt.%	0.324	1.763	1.872	2.003	3.038
2	29 wt.%	0.330	1.771	1.855	2.011	3.032
3	32 wt.%	0.333	1.777	1.862	2.012	3.016

As expected, increasing ignition loss was apparent with increasing solution throughput, since the majority of the heat available was consumed for evaporation of the water. The theoretical ignition loss of the pure Me nitrate mixture (anhydrous) is about 50% by weight. The deviations in the stoichiometry compared with the starting solution were ≤ 2% for all elements and test runs.

The morphology of the resultant particles was investigated by scanning electron microscopy (Fig. 1). Primary particles having a diameter of predominantly

between 1 and 10 μm with a hollow-ball, partly sponge-like structure were evident.

Example 2

In a further test run, the gas burner installed at the head of the reactor was operated with 6 m^3/h of hydrogen and air in a slightly super-stoichiometric ratio. The reactor jacket was again charged with 76 kg/h of air, but in this test run this was only warmed to 250°C, measured at the upper end of the annular space, by means of the electric air heaters. The solution was sprayed directly into the hydrogen flame at a mass flow of 5 kg/h by means of the two-component nozzle mentioned above for a period of 8 hours. The temperature between the reactor and the filter was on average 520°C. In this test run too, no deposits at all were evident on the reactor walls.

The powder was subjected to the same analyses as described in Example 1. The spoon test showed slight tracks in the surface of the spread-out powder, suggesting a few relatively hard agglomerates which had presumably partially melted in the hot flame. The remainder of the analyses show low ignition loss and a relatively large deviation of the stoichiometry of > 3 but < 5% compared with the starting solution. Both are attributed to more intensive warming of droplets in the hot flame.

Test run No.	Ignition loss	Pb	Bi	Sr	Ca	Cu
4	12 wt.%	0.327	1.785	1.827	1.961	3.099

Figure 2 shows a completely different morphology compared with Example 1. Irregular primary particles having a diameter in some cases well below 1 µm are agglomerated to form aggregates of varying strength.